

Benzyl Esters, Indoles and Carbazoles in Cigarette Smoke

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In a continuation of our work on chemical composition,¹ two aromatic esters previously unreported in tobacco smoke^{2,3} have been isolated from the smoke of commercial American cigarettes: benzyl benzoate and benzyl cinnamate. Also, confirmation of the presence of indoles and carbazoles in smoke has been obtained.

The compounds were found in the nitromethane-soluble fraction of the neutral substances. The fraction was obtained from one kilogram of smoke condensate (equivalent to 50,000 cigarettes) by the method previously described.⁴ Silicic acid chromatography of the nitromethane solubles yielded a fraction eluted with 1:1 n-hexane-benzene which had infrared spectral absorption consistent with a mixture of aromatic esters and amines or alcohols. Gas chromatographic analysis (1.2 m. \times 6 mm. o.d. column of 0.25% SE-30 on glass beads programmed at 4°C/min. from 65°C to 300°C) of the column eluate showed the presence of at least twenty peaks. One large peak eluted at 185°C and had an infrared and ultraviolet spectrum suggestive of an aromatic ester. The mass spectrum of the peak gave a parent mass of 212 and a fragmentation pattern characteristic of an aromatic ester. Saponification of the substance yielded benzyl alcohol and benzoic acid which were identified by gas chromatographic characteristics. Co-chromatography of the isolated substance and authentic benzyl benzoate gave a single peak. These data and the identical infrared and ultraviolet spectral characteristics of the isolated compound and benzyl benzoate confirmed the identity of the former. The level of the ester in smoke is at least four micrograms per cigarette.

Benzyl cinnamate and several indoles and carbazoles were isolated from the above silicic acid column eluate by subsequent chromatography on neutral alumina. Elution with 1:1 light petroleum-benzene yielded a fraction with spectral characteristics suggestive of an aromatic ester. Gas chromatographic examination of the eluate (2.4 m. \times 6 mm. o.d. column of 20% SE-30 on Chromosorb W at 180°C for 15 min. and then programmed at 8°C/min. to 265°C) showed three peaks eluting at 13, 26 and 34 min., respectively, the second of which was benzyl benzoate. The peak eluting in 34 min. was found to be benzyl cinnamate on the basis of chromatographic and spectral evidence essentially similar to that obtained for benzyl benzoate. The peak eluting in 13 min. has not been identified but

has spectral characteristics suggestive of an aromatic ether with an unsaturated side chain. The levels of benzyl cinnamate and benzyl benzoate in the smoke were approximately similar.

The indoles and carbazoles were eluted from the alumina column with benzene and, except for skatole, were not completely identified. Based on chromatographic and spectral characteristics, including mass spectrometric data, the following compounds are present: indole, skatole and monomethyl (other than skatole), dimethyl and trimethyl indoles; carbazole and monomethyl and dimethyl carbazoles. The presence of the indoles, carbazole and "methylcarbazoles" in cigarette smoke has been reported previously.⁵

Except for benzyl acetate in tobacco leaf, the presence of benzyl esters of aromatic acids in tobacco¹ or its smoke^{2,3} has not been reported. Although benzyl alcohol and benzoic acid are well-known leaf and smoke constituents, free or bound cinnamic acid has not been found therein; however, hydrocinnamic acid was recently isolated from cigar smoke in this laboratory.⁶ Since certain resins and essential oils presumably used as flavouring agents in commercial American cigarettes may be rich in esterified cinnamic acid⁷ and perhaps benzoic acid, the possibility that the isolated esters were derived from this source cannot be excluded. Regardless of the source, the esters are found in the smoke of such cigarettes and are potentially capable of exerting an organoleptic and/or other physiological effect.

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